

Orbitally-driven Peierls state in spinels

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(Dated: February 6, 2008)

We consider the superstructures, which can be formed in spinels containing on B-sites the transition-metal ions with partially filled t_{2g} levels. We show that, when such systems are close to itinerant state (e.g. have an insulator-metal transition), there may appear in them an orbitally-driven Peierls state. We explain by this mechanism the very unusual superstructures observed in CuIr_2S_4 (octamers) [1] and MgTi_2O_4 (chiral superstructures) [2] and suggest that similar phenomenon should be observed in NaTiO_2 and possibly in some other systems.

PACS numbers: 71.30.+h, 71.28.+d, 75.25.+z

Systems with complicated lattices, such as pyrochlore-type lattice of corner-sharing tetrahedra in spinels, often display complicated types of ordering. The best known example is magnetite Fe_3O_4 , which apparently has charge ordering below Verwey transition at $T_V = 120$ K, the detailed type of ordering still being a matter of hot debate [3]. Recently two other examples of exotic types of ordering were observed by Radaelli and coworkers: octamer ordering in CuIr_2S_4 [1] and helical (or chiral) distortion in MgTi_2O_4 [2]. In all three cases, superstructures appear in the insulating phase below metal-insulator transition; in CuIr_2S_4 and MgTi_2O_4 , it is accompanied by the formation of nonmagnetic state (spin singlet on a dimer). The origin of these strange and beautiful structures was not clarified in [1, 2]

Below we suggest a very simple explanation of the superstructures in CuIr_2S_4 and MgTi_2O_4 , using the concept of *orbitally-driven Peierls state*. We show that the specific features of orbitals involved, on the pyrochlore lattice of B-sites of spinels, lead to the formation of essentially one-dimensional bands and, with proper filling, lead to the Peierls-like effect, which in these particular cases has a form of tetramerization along certain directions. Viewed from different perspective, the resulting states give just the octamer ordering of Ref. [1] and chiral ordering of Ref. [2]. Using the same concept, we predict also that similar phenomenon should exist in some other materials, e.g., in NaTiO_2 and possibly in V spinels.

In both CuIr_2S_4 and MgTi_2O_4 , the transition-metal (TM) ions Ir and Ti are located in almost regular S_6 and O_6 octahedra, so that the dominant crystal field (CF) splits the d -levels into the t_{2g} triplet and e_g doublet. In both cases, only t_{2g} levels are occupied, by one electron in Ti^{3+} and by five or six electrons in Ir^{4+} and Ir^{3+} respectively (average Ir valence is +3.5). The shape of these orbitals is such that the strongest overlap in the elementary Ir_4S_4 or Ti_4O_4 cubes is between the same orbitals along the particular direction, e.g., xy with xy -orbitals for the TM pair in the xy -plane, or yz with yz -orbitals

for the pair in the yz -plane, see Fig. 1. Thus the dominant hopping will be along the straight TM-TM chains, which would lead to formation of one-dimensional bands with the dispersion $E(k_\alpha) = -2t\cos k_\alpha$ where α denotes the direction along corresponding chain. This orbital-dependent hopping will play crucial role in our explanation.

We start by discussing the case of CuIr_2S_4 . In this system, below the metal-insulator transition temperature T_{MI} , there appears the net tetragonal distortion (elongation, $c/a = 1.03$ [4]), and besides that, the complicated octamer structure appears [1]: Ir^{3+} and Ir^{4+} order in octamers, and in the Ir^{4+} octamers there appears also an alternation of short and long bonds, see Fig. 2 in [1]. This beautiful structure seems extremely unusual. However the situation is much simpler if one looks at what happens in the *straight Ir chains*: one immediately notices that in five out of six such chains there appears a tetramerization — an alternation $\text{Ir}^{3+}/\text{Ir}^{3+}/\text{Ir}^{4+}/\text{Ir}^{4+}/\dots$, and in one of them — corresponding dimerization, see Fig. 2(a).

One can naturally explain this pattern if one looks at the electronic structure of this compound, schematically shown in Fig. 2(b). Due to tetragonal elongation, there will appear a CF splitting of t_{2g} levels, and besides (which is probably more important), the xy band will become broader. With the 5.5 electrons (or 0.5 hole) per Ir in these levels, the lowest two bands will be fully occupied, and the upper xy one-dimensional band will be 3/4-filled. Thus we can expect a Peierls or charge density wave (CDW) transition, accompanied by tetramerization in the xy chains [along the (1, 1, 0) and (1, -1, 0) directions], with holes in the xy orbitals, as shown in Fig. 2(a). As is seen from this figure, the resulting state exactly corresponds to the one found in [1]: Ir^{3+} and Ir^{4+} form octamers. Besides, the Ir^{4+} pairs in the xy chains have orbitals directed towards one another, thus these pairs will form spin singlets. When we release the lattice, corresponding bonds will become shorter, again consistent with the structure of [1]. Thus the explanation of this ap-

parently very complicated structure becomes extremely simple and natural if we look at it from the point view of straight Ir chains, which, for this orbital occupation, form natural building block in spinels.

The same idea explains also the chiral superstructures observed in MgTi_2O_4 [2]. Below T_{MI} at 260 K, a tetragonal distortion (here contraction) appears also in this system, together with the inequivalent bonds, so that, if one connects short and long bonds, they form spirals along the c - or z -direction, which may be both left- and right-moving. Apparently, on the short bonds, Ti-Ti pairs form spin singlets which is rather typical for d^1 configurations. This naturally explains the drop of magnetic susceptibility below T_{MI} [5]. And again this superstructure, the origin of which looks very puzzling, can be explained very easily if one looks at the situation in the *straight Ti chains*. One immediately notices that in all chains running in the $(0, 1, 1)$, $(0, 1, -1)$, $(1, 0, 1)$, and $(1, 0, -1)$ directions (lying in the zx - and yz -planes) one has the *tetramerization*: an alternation of short/intermediate/long/intermediate/... bonds. This structure can be naturally explained if we look at the electronic structure of this system, Fig. 3(b). In the high temperature phase, Ti^{3+} ions have one electron in the triply-degenerate t_{2g} level, which in the tight-binding scheme would give three one-dimensional degenerate bands (we neglect here small trigonal splitting). One can reduce the band energy by tetragonal distortion — the effect similar to the band Jahn-Teller effect invoked by Labbe and Friedel to explain the cubic-tetragonal transition in A15 compounds (V_3Si , Nb_3Sn) [6]. The tetragonal compression observed in MgTi_2O_4 would increase the bandwidths of the zx and yz bands and decrease that of the xy band, opposite to the case of CuIr_2S_4 . With one electron per Ti, the lowest doubly degenerate zx and yz bands will be $1/4$ -filled. This would lead to the usual instability and to the formation of superstructure with the wave vector $Q_\alpha = \pi/2$, i.e. to a tetramerization in the zx - and yz -directions, in accordance with the experiment. In contrast to the usual Peierls transition, we even do not have here to move ions: one can get corresponding superstructure by changing orbital occupation of respective ions (we may call it a ODW — orbital density wave).

Such ODW will be stabilized by the electron repulsion. In the strong-coupling limit we would get in each of these chains the orbital ordering of the type $zx-zx-yz-yz-zx-zx$..., see Fig. 3 (this ordering satisfies the "Anderson rule": there will be two orbitals of each type in each Ti tetrahedron). Of course the lattice would then follow: strong overlap of the orbitals in the pair with the lobes along corresponding chains would lead to the alternation of strong (short)-intermediate-weak(long)-intermediate bonds in each chain, with the spin-singlet states at short bonds. If now one connects short with long bonds, one gets the helical pat-

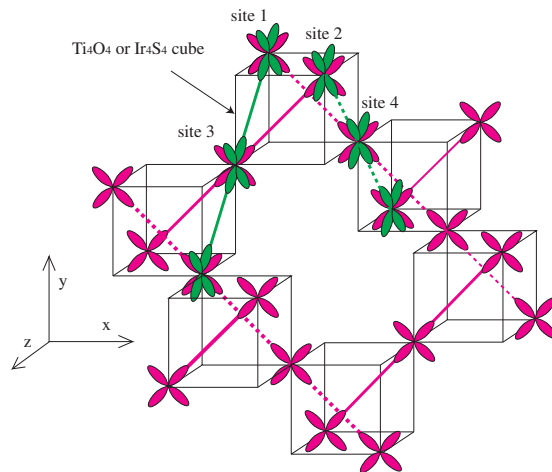


FIG. 1: Orbital dependent hopping in the pyrochlore lattice of spinels. For an electron in the xy orbital of site 1, the dominant hopping is along the $(1, -1, 0)$ direction in the xy plane (to the site 4). On the other hand, for an electron in the xy orbital of site 2, the dominant hopping is along the $(1, 1, 0)$ direction in the xy plane (to the site 3). The $(1, 1, 0)$ chains shown by the red solid line never crosses the $(1, -1, 0)$ chains shown by the red broken line. For electrons with the yz orbitals of site 1 and 2, the dominant hopping is along the $(0, 1, -1)$ and $(0, 1, 1)$ directions (to the sites 3 and 4, respectively).

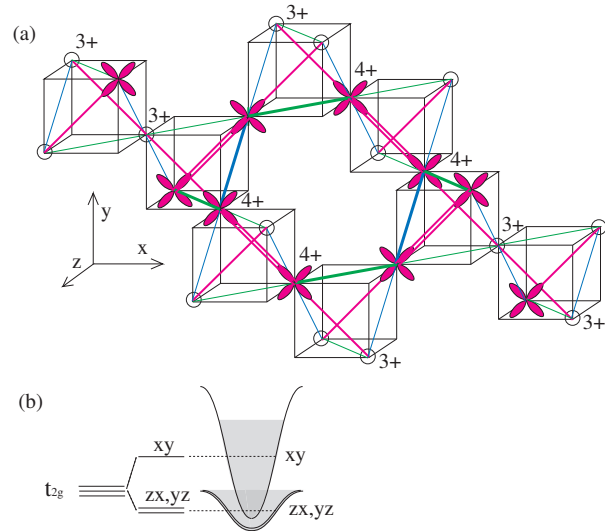


FIG. 2: (a) Charge and orbital ordering in CuIr_2S_4 . Octamer is shown by thick lines, short singlet bonds — by double lines. (b) Schematic electronic structure of CuIr_2S_4 .

tern stressed in [2]. Thus one can visualize the structure observed in [2] both as a bond alternation and as a site-centered orbital ordering. Here we considered tetragonal transition (band Jahn-Teller effect) and orbitally-driven Peierls distortion separately, but in reality they occur simultaneously, so that it is the total energy gain which stabilizes this structure.

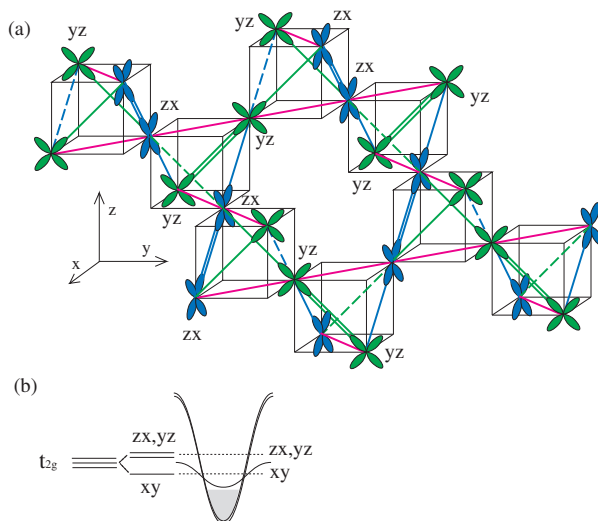


FIG. 3: (a) Orbital ordering in MgTi_2O_4 . Short singlet bonds are shown by double, intermediate — single, and long — dashed lines. yz orbitals are shown by green and zx orbitals — by blue. (b) Schematic electronic structure of MgTi_2O_4 . Note different orientation of coordinate axes as compared with Figs.1,2

The situation in MgTi_2O_4 is somewhat more complicated than that in CuIr_2S_4 : whereas in the latter both the local CF splittings and the change of the bandwidths combine to make only xy band partially occupied, in MgTi_2O_4 these two effects oppose one another. Apparently the band Jahn-Teller effect here dominates leading to the tetragonal elongation instead of compression which would be more favourable for localized electrons. One can make crude estimate, which shows that one gains much more kinetic energy with this filling (almost $0.5t$, where t is the nearest-neighbour hopping) when one occupies doubly-degenerate bands close to the bottom (which happens at distortion with $c/a < 1$) than if one would have an opposite distortion and would occupy nondegenerate xy band. But the most direct confirmation of our picture comes from the band-structure calculations presented in Ref.[2]: according to them below T_c in MgTi_2O_4 indeed only the zx and yz bands are occupied.

One can argue that similar phenomenon should exist in other materials, e.g. in NaTiO_2 with the triangular two-dimensional lattice of Ti^{3+} ions. This material also has a metal-insulator transition with structural distortion at 250K, which leads to a rather strong elongation of TiO_6 octahedra along one of the local pseudocubic axes [7] (which, in combination with the original rhombohedral structure, makes the system monoclinic). The resulting situation may then become similar to that in MgTi_2O_4 , and one can expect the formation of similar superstructure with the alternation of zx - zx - yz - yz - zx - zx -... orbitals along two sets of Ti chains running along the distortion axis, with the formation of corresponding

spin-singlet states. The drop of susceptibility was indeed observed in NaTiO_2 below T_c [7], but the predicted superstructure was not yet seen.

The situation may be also similar in V spinels MV_2O_4 , $M = \text{Mg}, \text{Zn}, \text{Cd}$ [8, 9]. All of them have cubic-tetragonal transitions with $c/a < 1$, which lead to the splitting of t_{2g} levels with the low-lying xy singlet and higher zx , yz doublet. With two electrons per V ion, we would have the situation resembling that of Ti: one electron would occupy the xy orbital, but the second one would be in the doubly-degenerate (zx , yz) orbitals or bands (note that this distortion ($c/a < 1$) is again "anti-Jahn-Teller": Jahn-Teller effect for localized electrons would rather lead to the opposite distortion, with both electrons in the lower doublet). Consequently, one may expect the formation of the superstructure similar to that discussed above. Recent results [9] confirm the presence of one-dimensional spin chains made by the xy -electrons, and show some indirect evidences of superstructure in the c - or z -direction, which, however, the authors interpret as dimerization (alternation of planes with zx and yz orbitals, see also [10]). More detailed structural studies should clarify which structure is actually realized in these systems.

And finally, the same effect may be relevant in magnetite, at least partially. The most recent structure proposed for Fe_3O_4 [11] (shown in Fig.7 of [11]) has certain similarities with the structures discussed above: there is also a tetramerization in zx - and yz -chains, but of somewhat different type than that in CuIr_2S_4 : in two out of four such chains we have the same pattern, $\text{Fe}^{2+}/\text{Fe}^{2+}/\text{Fe}^{3+}/\text{Fe}^{3+}/...$, but in two others the tetramerization is of different type: in one $2+/2+/2+/3+/2+/2+/2+/3+/...$ and in another $3+/3+/3+/2+/3+/3+/3+/2+/...$. According to LDA+ U calculations [12], there appears also an orbital ordering in this structure, such that again only two types of orbitals zx and yz (or their combinations) are occupied by the extra t_{2g} electron of Fe^{2+} . It is not yet clear to us whether the effects studied above play a role in this ordering in magnetite, but the analogy is rather suggestive.

Actually, the situation with orbitally-driven Peierls state leading to spin singlets is not unique for spinels or systems with triangular lattices like in NaTiO_2 [13]. Such phenomenon was also observed in pyroxene $\text{NaTiSi}_2\text{O}_6$ [14]. One can also argue that the same effect — orbitally-driven singlet pair formation — occurs also in the recently synthesized $\text{La}_4\text{Ru}_2\text{O}_{10}$ [15]. The explanation given in Ref. [15] (transition to a zero-spin Ru^{4+} state) seems rather unlikely, as it would require CF splitting of Ru t_{2g} levels exceeding the on-site Hund's rule energy, which seems rather improbable. Rather, one can suggest that the nonmagnetic ground state of $\text{La}_4\text{Ru}_2\text{O}_{10}$ is also caused by the orbitally-driven spin singlets. Recent neutron scattering results on single crystalline $\text{La}_4\text{Ru}_2\text{O}_{10}$

[16] may indeed agree with this interpretation. Thus there appears more and more systems in which an orbital ordering leads to a singlet Peierls state.

Summarizing, we argue that the complicated superstructures observed recently in some spinels (CuIr_2S_4 and MgTi_2O_4) are naturally explained as an orbitally-driven Peierls distortion, caused by the proximity to an itinerant state. We predict similar phenomenon in NaTiO_2 , and possibly in some other systems.

We are grateful to P. Radaelli, S.-H. Lee and R. Osborn for useful discussions.

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